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ANALYSIS OF SULFUR IN FUEL OILS BY ENERGY-DISPERSIVE X-RAY FLUORESCENCE

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Technical Paper No. 15
Annapolis Field Office
Region III
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16. ABSTRACT

Energy dispersive x-ray fluorescence was used to analyze for sulfur in oil in commercially prepared standards, NBS standards and laboratory samples. The technique of energy dispersive x-ray fluorescence for sulfur was found to be accurate, precise, and required minimal sample preparation. In addition it was non-destructive, and enabled the simultaneous determination of sulfur and its interfering elements: phosphorus; zinc; barium; calcium; and chlorine.

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INTRODUCTION

Sulfur oxides have long been recognized as significant air pollutants. With increased usage of sulfur containing fuels, an increase in atmospheric sulfur dioxide content will become an ever more important problem. Legislation has been passed governing the allowable levels of sulfur in fuels in an attempt to control this source of air pollution.

Energy-dispersive x-ray fluorescence (EDXRF) can provide a rapid, non-destructive method of analysis of sulfur in fuel oils. Because the EDXRF system is automated and minimal sample preparation procedures are involved, a reduction in the time and cost of analysis is possible.

EXPERIMENTAL

Materials

Sulfur standards of: 2.14, 1.05, 0.268, and 0.211 weight percent sulfur in fuel oil were obtained from the National Bureau of Standards. In addition, sulfur standards prepared by commercial sources were obtained with concentrations in weight percent sulfur of: 2.02, 1.06, and 0.49. Actual samples analyzed by wavelength-dispersive x-ray fluorescence with the following weight percent sulfur concentrations were also analyzed: 2.95, 2.10, 2.05, 2.00, 1.61, and 0.33. Zinc, barium, and lead standards were prepared from Conostan Metallic-Organic standards.

Equipment

A Finnigan 900 Series energy dispersive x-ray fluorescence spectrometer and data system were used for all EDXRF analyses.

Procedure

The determination of sulfur in fuel oils follows the procedure outlined in ASTM D2622-67[1]: Standard Method of Test for Sulfur in Petroleum Products (X-Ray Spectrographic Method) with minor changes in the procedure to accommodate the energy dispersive equipment. A brief outline of the procedure follows:

a. Place the sample in an open cell sample cup over which 0.25-mil Mylar film has been stretched and attached with a snap-on ring. Attach microporous film to the open-end of the sample cup to prohibit the oil from escaping.

b. Place the samples in the x-ray beam, apply vacuum, and allow the atmosphere in the x-ray chamber to come to equilibrium. Instrument operating conditions are found in Table III.

c. Determine the intensity of the SK_{α} peak at 2.307 Kev and make background measurements adjacent to the peak.

d. If the sample contains interfering elements in concentrations greater than those listed in ASTM D2622-67, dilute the sample by weight with white oil.

Calibration

a. Determine the net SK_{α} intensity for all standards and samples.

b. Determine the weight percent sulfur by ratio against the 2.14 weight percent sulfur standard reference material using net intensities or by comparison to a calibration curve of sulfur net intensity vs. concentration.

c. Measure a sensitivity standard at frequent intervals and determine the net counting rate for each sample.

RESULTS AND DISCUSSION

Commercially obtained standards, NBS standards, and previously analyzed field samples were analyzed by energy dispersive x-ray fluorescence. The accuracy results shown in Table I and precision results shown in Table II, indicate the high degree of precision and accuracy obtainable by this method of analysis. The average recovery was 97% (Table I) and a plot (Figure I) of found weight percent sulfur vs. known weight percent sulfur gives a correlation coefficient of 0.999. A paried-t test applied to the data indicates that there is no difference between the found and known values at a 95% confidence level. An average standard deviation of 0.02 weight percent sulfur was found over the 0.16 to 2.00 weight percent sulfur range. A plot of the standard calibration curve (Figure II) is linear with a correlation coefficient of 0.9997, further facilitating analysis by this method.

The minimum detectable amount[2], defined as 3x(intensity of the background)$^{1/2}$, is 0.11 weight percent sulfur; this is below the majority of legislated limits of sulfur concentration in fuel oil in the United States[3].

The analysis of fuel oil samples by energy-dispersive x-ray fluorescence is accurate and precise, requires minimal sample preparation, and is non-destructive. It also simultaneously determines sulfur and its interfering elements, phosphorus, zinc, barium, calcium, and chlorine. These factors combine to produce an overall increase in the efficiency of analysis of sulfur in fuel oils.

TABLE I

Comparison of Sulfur Results Found by Classical and EDXRF Methods

Date of Analysis	Origin	Classical wt. % S	EDXRF wt. % S	% R*
10-28-75	Field Sample	2.95	2.98	101.0
	Field Sample	2.10	2.07	98.6
	Field Sample	2.05	2.05	100.0
	Secondary Std.	2.02	1.94	96.0
	Field Sample	2.00	2.04	102.0
	Field Sample	1.61	1.68	104.3
	Secondary Std.	1.06	0.99	93.4
8-12-76	Field Sample	2.94	3.04	103.4
	Field Sample	2.10	2.13	101.4
	Field Sample	2.00	2.04	102.0
	Field Sample	1.61	1.67	103.7
2-11-77	Secondary Std.	1.06	1.01	95.3
	NBS	1.05	1.04	99.0
	Secondary Std.	0.49	0.48	98.0
	NBS	0.268	0.264	98.5
	NBS	0.211	0.206	97.6
2-14-77	NBS	1.05	1.02	97.1
	NBS	0.211	0.155	73.4
4-27-77	Secondary Std.	1.06	1.00	94.3
	NBS	1.05	1.06	101.0
	NBS	1.05	1.03	98.1
	NBS	0.268	0.231	86.2
	Secondary Std.	0.24	0.22	91.7
	NBS	0.211	0.192	91.0

correlation coefficient = .999

mean = 97. %

s = 6.7%

t-statistic = .540

degrees of freedom = 23

*R = Recovered

Figure I: Plot of Found Weight Percent Sulfur vs Known Weight Percent Sulfur

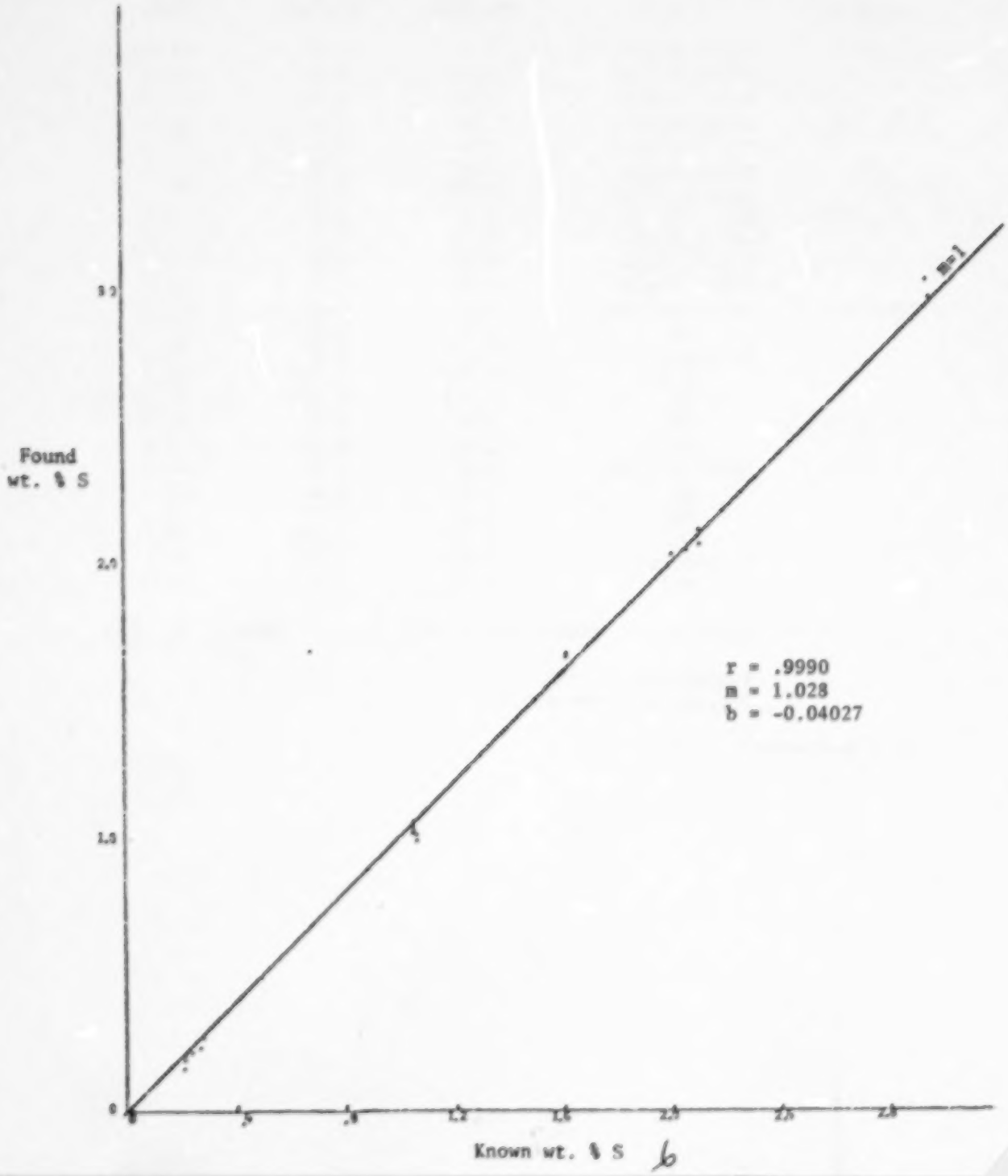


TABLE II

Results of Duplicate Analyses of Field Samples

Range	Duplicate I wt. % S	Duplicate II wt. % S	difference
< 0.3%	.16	.17	.01
	.16	.17	.01
	.16	.19	.03
	.16	.21	.05
	.16	.17	.01
		s = .02% S	
0.3-1.0%	.72	.72	0
	.96	.98	.02
	.99	.98	.01
	.93	.91	.02
	.59	.58	.01
	.44	.44	0
		s = .01% S	
> 1.0%	1.99	1.92	.07
	1.03	1.01	.02
	1.04	1.00	.04
	1.05	1.04	.01
	1.74	1.74	0
	1.09	1.08	.01
	.96	.94	.02
	1.63	1.63	0
		s = .02% S	

$s = (\Sigma(d^2) / 2k)^{\frac{1}{2}}$

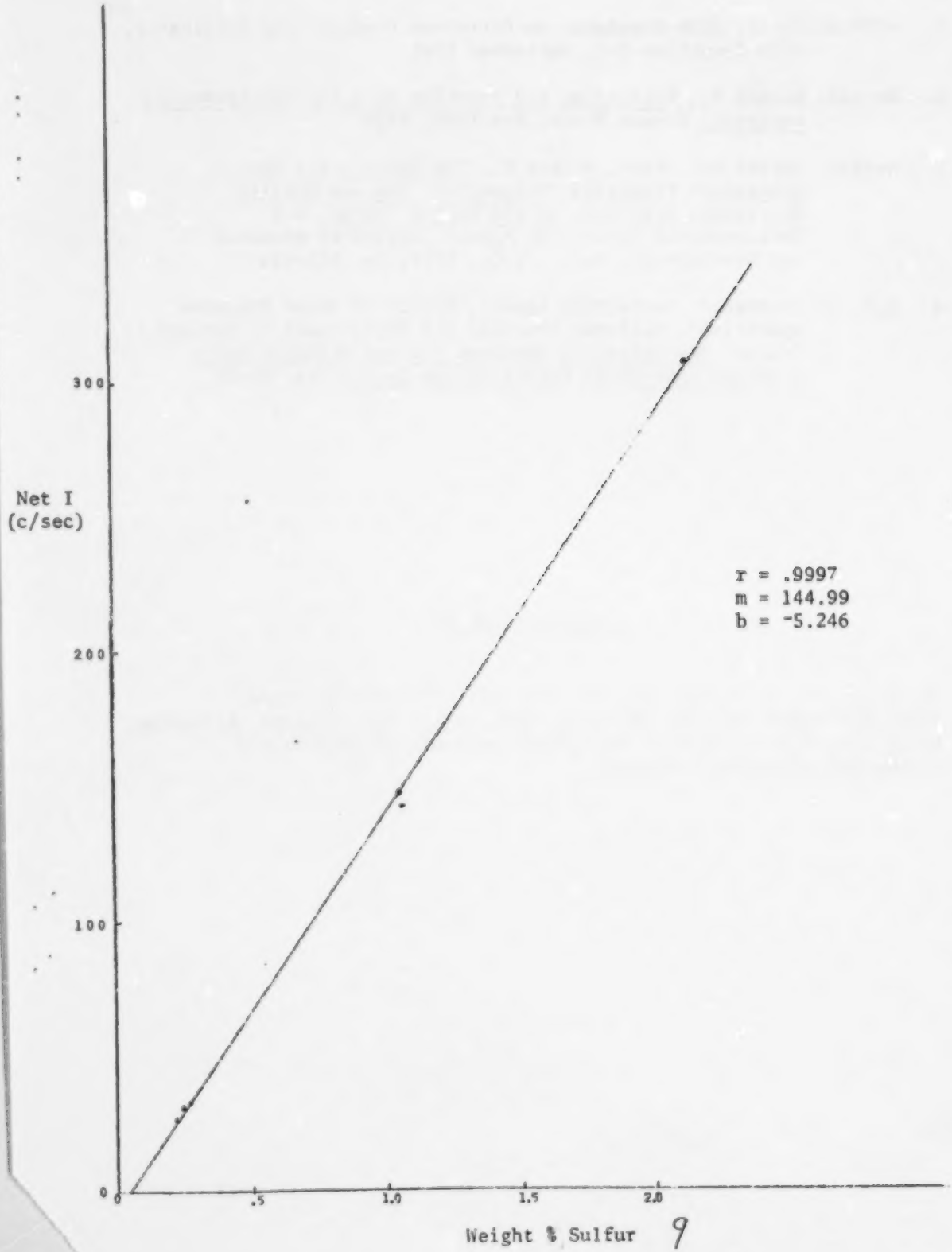
where: s = standard deviation[4]
d = difference between duplicates
k = number of samples

TABLE III

Instrument Operating Conditions

Date of Analysis	Voltage Kv	Amperage ma	Time sec	Path	Filter	Collimator diameter mm
10-28-75	10	4	500	vacuum	none	1
8-12-76	10	1	500	vacuum	none	6
2-11-77	10	0.8	500	vacuum	none	6
2-14-77	10	0.8	1000	vacuum	none	6
4-27-77	10	0.8	1000	vacuum	none	6

Figure II: Plot of SK_α Net Intensity vs Weight Percent Sulfur



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